The Catalytic Effect of Soda on the Reaction between Steam and Carbon from the Pyrolysis of Low Grade Oils

BY
MARTIN A. ELLIOTT

A DISSERTATION
SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
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THE catalysis of the reactions between carbon and carbon dioxide and between carbon and steam is of considerable practical interest, and the patent art extends at least as far back as 1867 (*13*). With developments in synthetic hydrogen production and the advance of scientific research in gas engineering, these catalyses have received considerable attention from workers in this country and abroad since the World War, and the accelerating effects of a number of substances such as the alkali and alkali earth bases, and of certain alkaline compounds from the iron group have been well established (*1*, *2*, *8*, *9*, *11*, *12*). A recent American paper (*4*) seriously proposes the commercial merits of sodium carbonate as an aid in producer-gas making but holds that the high production of carbon monoxide during the blasting period with attending potential heat loss would render the use of such a catalyst in water-gas manufacture undesirable.

While this may be true for the generator carbon, the same considerations do not apply to the carbonaceous deposits left in the checker brick of the carbureted water-gas machine, since this relatively inert material may be largely lost for gas-making purposes. Moreover, as its deposition may occur chiefly during an oil injection period coincident with an early portion of the steam run, catalysis presents the attractive possibility that much of this carbon may be gasified before the blasting phase begins, thus minimizing potential heat losses. The gasification of the relatively inert carbonaceous matter deposited by the oil has achieved added importance

with the wide use of low-grade, high-carbon residuum oils, such as Bunker C, as carbureting agents in American water-gas practice. Because of the sluggishness of the steam-carbon reactions at the temperature of the carburetor, American practice ordinarily depends upon combustion with air for the removal of such deposits (*6, 7, 10*), and some processes secure favorable temperature levels by throwing heavy oil directly on to the fire (*3*).

Such considerations indicated that it would be desirable to investigate the catalysis of the gasification with steam of the heavy oil carbon as deposited on checker brick surfaces at temperatures encountered in water-gas practice. The ex-

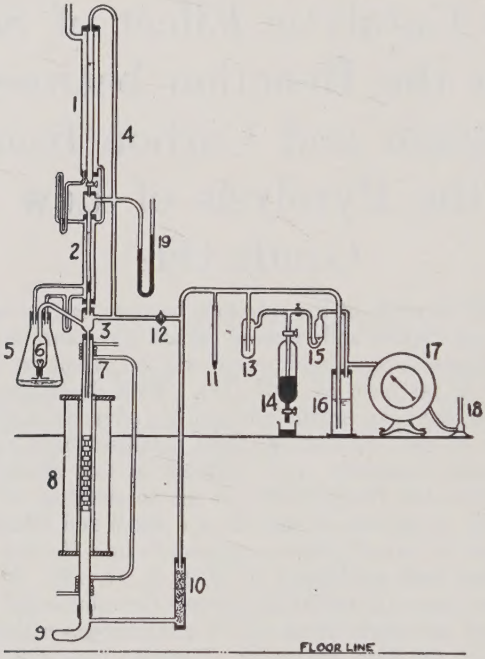


FIGURE 1. DIAGRAM OF APPARATUS

perimental work to be described was planned for this purpose. Among other differences, this work, unlike some prior studies, did not involve premixing to secure intimate contact between carbon and catalyst.

EXPERIMENTAL PROCEDURE

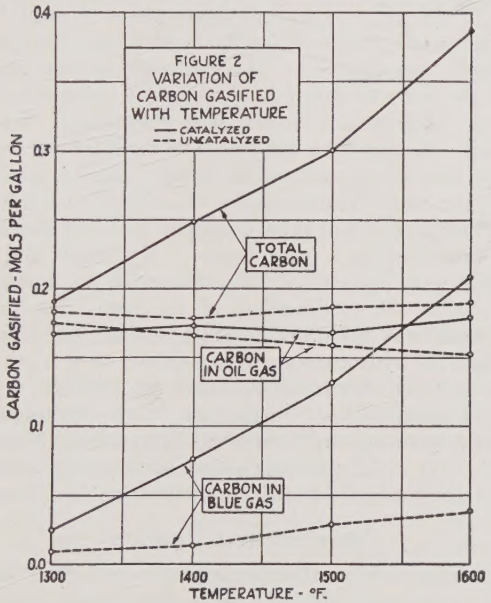
A diagram of the apparatus employed is shown in Figure 1.

Essentially, this provided means for the delivery, at predetermined rates, of steam and a viscous petroleum residuum oil to heated refractory surfaces, untreated or impregnated with sodium carbonate or other catalytic materials. Facilities, 9, 10, were arranged for removing and collecting the tar from the gas

produced, for sampling the gas, 14, and, after removal of its corrosive impurities, for metering it, 17. The oil rate, about 0.2 cc. (0.000053 gal.) per minute, was controlled by keeping a constant head of oil on a small capillary tube, 2. To maintain it at a uniform and constant temperature, and at the same time to reduce the oil viscosity so that it would flow easily, all of the oil-feeding equipment was steam-jacketed.

The steam rate was controlled by regulating the current input to an immersed platinum heating coil of known resistance. The vaporizer, 6, was jacketed with boiling water, so that the immersed coil supplied only the latent heat of vaporization. About 0.15 gram (0.00033 lb.) of steam per minute was fed to the reaction tube.

This tube, $^{13}/_{16}$ inch (2.1 cm.) internal diameter and 42 inches (106.7 cm.) long, was made of the chromium-steel alloy known as Allegheny metal. Silica and porcelain tubes are subject to attack by alkali and were therefore deemed unsatisfactory. Comparative experiments were, however, made with this and a



silica tube and showed only slight differences. The tube was heated electrically as shown, 8, and the ends water-cooled, 7, to permit the attachment of other parts of the apparatus. Tar and condensed steam were collected in a trap, 9, at the bottom of the apparatus. Tar fog was removed by a cotton filter, 10. The gas sample was collected over mercury in a Frazer and Hoffman sampling tube, 14. In the uncatalyzed experiments, a caustic soda scrubber, 16, was used to remove carbon dioxide and hydrogen sulfide before it passed to the meter. This scrubber was by-passed around the sampling tube and the gas was scrubbed with cadmium acetate, 13, before sampling. In the catalyzed experiments, a cadmium acetate scrubber was substituted for the caustic scrubber because of the greater quantity of carbon dioxide produced.

Small magnesia blocks, $^{11}/_{16} \times {}^{3}/_{8} \times {}^{1}/_{2}$ inch (17.5 × 9.5 × 12.7 mm.), were sawed from commercial magnesia brick sup-

plied by the Harbison-Walker Company to furnish the refractory surface. To insure analogous conditions, the same blocks were used in all comparative experiments, the carbon being burned off at the conclusion of each. When the effect of soda was studied, the blocks were impregnated with 5 per cent of their weight of sodium carbonate. After each catalyzed experiment, they were leached with hot water and then reimpregnated. Once impregnated, they were never again used in an uncatalyzed experiment.

The oil was supplied by the Baltimore Branch of the Standard Oil Company of New Jersey. It was a Bunker C oil containing 1.6 per cent sulfur and gave 13 per cent coke.

After the reaction tube had been brought to the desired temperature it was purged for about 10 minutes with steam. Oil was then admitted at the predetermined rate. The collection of the gas sample was begun about 20 minutes after the oil admission and was discontinued 10 minutes before the experiment was stopped. The hydrogen sulfide concentration of the gas was determined while the experiment was in progress. Before and after each experiment the steam vaporizer, cracking tube, tar trap, and tar filter were weighed.

In the gas, the percentages of carbon dioxide, illuminants, and oxygen were determined by absorption, using an Orsat of the Bureau of Mines type, equipped with automatic pipets (to be described in a later paper). Hydrogen and carbon monoxide were determined by preferential combustion over copper oxide. A modification of the usual handling with copper oxide was found desirable (to be described elsewhere). The saturated hydrocarbons were assumed to be methane and ethane, and were determined by slow combustion.

The composition and heating value of the illuminants were calculated according to the method proposed by Watson and Ceaglske (*14*) which involves a slow combustion of a portion of the original sample in addition to the usual analytical data.

Experimental Results

Preliminary comparative experiments at about 1650° F. (899° C.) with and without impregnated refractories showed marked increases in the blue gas generation, the carbon gasified, the thermal yield, and a reduction in the percentage of carbon deposited when the refractory was impregnated with sodium carbonate.

With this encouragement, experiments were performed to determine the catalytic effects at checker chamber temperatures encountered in the commercial production of carbureted water gas. No attempt was made, however, to dictate experimental conditions favorable to efficient oil cracking, and, in fact, a large deposition of carbon, at least in the uncatalyzed experiments, was desired.

Gasification of Carbon

The increased gasification of carbon resulting when the

refractory was impregnated with sodium carbonate is shown in Figure 2. Although this increase was only slight at 1300° F. (704° C.), it became more marked at the higher temperatures, thus at 1600° F. (871° C.) about twice as much carbon was gasified when the refractory was impregnated with soda. The carbon appearing as the monoxide and dioxide is designated as the carbon in the blue gas. The curves in Figure 2 show that the increased gasification found in the catalyzed experiments is due chiefly to the production of greater quantities of blue gas. Thus, at 1600° F. (871° C.), 86 per cent of the increase in the total carbon gasified was due to the increase in the amount of carbon appearing as the monoxide and dioxide.

TABLE I. VARIATION OF STEAM DECOMPOSITION WITH TEMPERATURE IN CATALYZED AND UNCATALYZED EXPERIMENTS

TEMP.	MASS VELOCITY OF STEAM[a]	MASS VELOCITY OF OIL[a]	STEAM PER GAL. OIL	STEAM DECOMPOSITION
° F.	*Lb./sq. ft. free cross section/hr.*	*Lb./sq. ft. free cross section/hr.*	*Lb.*	%
		UNCATALYZED		
1300	11.2	13.9	6.3	5
1400	10.5	14.1	5.9	6
1500	11.1	13.7	6.4	12
1600	11.6	13.5	6.8	15
		CATALYZED		
1300	10.3	13.5	6.0	13
1400	7.9	12.6	5.0	41
1500	9.3	13.7	5.4	62
1600	11.2	12.7	7.0	67

[a] Free cross-section area = 0.00181 square foot; volume of free space = 0.00393 cubic foot.

The variations in the steam decomposition in the catalyzed and uncatalyzed experiments are shown in Table I. When the catalyst was present, the percentage of steam decomposed rose markedly at the higher temperatures.

As would be expected, the increased carbon in the blue gas was accompanied by a decreased deposition of carbon, and at 1600° F. (871° C.) the refractory at the conclusion of the catalyzed experiment was practically free from carbon; in the uncatalyzed experiments little variation was noted in the quantity of blue gas and amount of carbon deposited over the temperature range studied.

When the refractory was impregnated with soda, slightly more carbon appeared as methane, ethane, and illuminants, designated in Figure 2 as carbon in the oil gas.

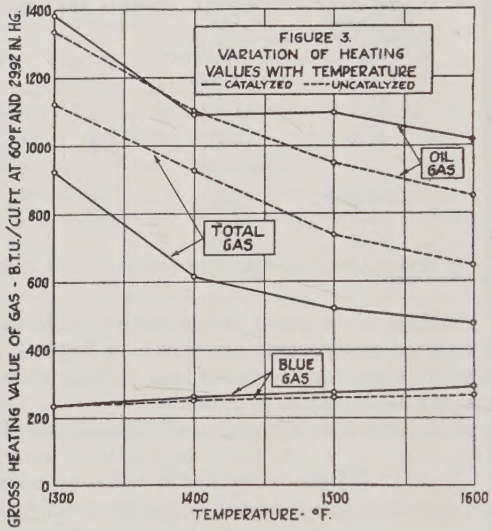
VARIATIONS IN HEATING VALUE

The variations in the heating value of the gas made are shown in Figure 3. Because of the increased blue gas generation with the impregnated refractory, the heating value per unit volume of total gas decreased, but, as this decrease in calorific value was not as rapid as the increase in the total volume of gas generated, the thermal yield from the oil increased when the catalyst was present. In the calculations,

the total of the hydrocarbon gases and hydrogen, corrected for the hydrogen corresponding to the carbon oxides of the blue gas, was designated as the oil gas. It will be noticed that only slight differences in the heating value of the oil gas were observed in the catalyzed and uncatalyzed experiments at 1300° F. (704° C.) and 1400° F. (760° C.). At higher temperatures, the thermal content of the oil gas was noticeably greater when the refractory was impregnated with the catalyst, and this increase was accompanied by a decrease in the quantity of oil gas obtained per gallon of oil. This suggests less extensive pyrolysis in the catalyzed experiments and will be discussed later.

Thermal Yields

The thermal yields, per unit of oil decomposed, are shown in Figure 4. While no difference is shown in the total yield at



1300° F. (704° C.), at the higher temperatures decided increases in thermal yield were found in experiments in which the refractory was impregnated with soda. Thus at 1400° F. (760° C.) the increase amounted to about 25 per cent, and at 1600° F. (871° C.) the increase was about 62 per cent. These increases were due to the greater thermal yields from the blue gas, as shown in Figure 4.

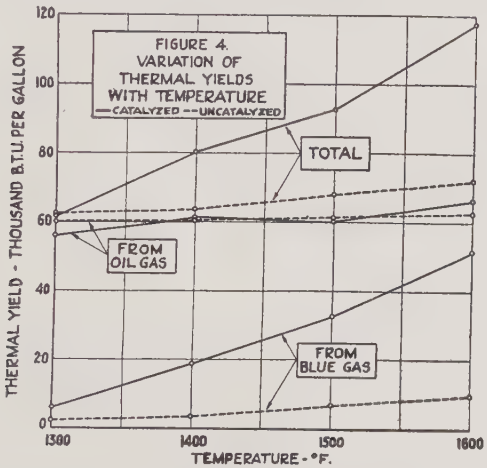
Influence of Catalyst on Pyrolysis of Oil

As shown, at the same temperatures, wide variations in the composition and quantity of the gas produced and the quantity of the steam decomposed were found between the catalyzed and uncatalyzed experiments. Because of these variations, the conditions governing the pyrolysis of the oil were

different, making it impossible to determine whether the variations noted in the oil gas composition resulted from the direct action of the catalyst or from the secondary effects due to the changed conditions. In the catalyzed experiments, the increased partial pressure of the hydrogen and carbon monoxide, for example, favored the production of a high-quality oil gas.

The quantity of tar formed per gallon of oil was approximately the same in both the catalyzed and uncatalyzed experiments at the same temperature. The absolute amount of tar formed was so small that it was not deemed advisable to attempt an analysis.

To secure more information upon the direct influence of the catalyst upon the pyrolysis of oil, catalyzed and uncatalyzed experiments were carried out at 1600° F. (871° C.) in which blue gas was added in the uncatalyzed experiment in such an amount that the total gas issuing from the cracking tube



per unit oil input was the same as that in the catalyzed experiment. The observations are compiled in Table II. The thermal yield and the yield of the gaseous hydrocarbon constituents were approximately the same in both catalyzed and uncatalyzed experiments performed under comparable oil cracking conditions. So far as may be judged from this evidence, under these experimental conditions the soda was without any marked effect upon the pyrolytic reactions.

Character of Illuminants

In the laboratory experiments the illuminants were found to be predominantly olefinic in character as shown by the hydrogen-carbon ratios summarized in Table III. Under identical conditions, the variations in these ratios amounted to about 5 per cent. The decrease with increasing temperature is, of course, to be expected. The explanation for the

slightly lower hydrogen-carbon ratios noted in the catalyzed experiments over the entire temperature range is not clear.

The minimum heating value for the illuminants was noted at about 1500° F. (816° C.), the carbon and hydrogen content per unit volume decreasing as the temperature was raised from 1300° F. (704° C.) to 1500° F. (816° C.). The formation of additional aromatics may be responsible for the rise in this content from 1500° F. (816° C.) to 1600° F. (871° C.).

Although the differences in the composition and heating value of the illuminants between the catalyzed and uncatalyzed experiments were very small at the lower temperatures, a marked difference was observed at 1600° F. (871° C.).

It is evident that the net variation in the experimental conditions produced by the catalyst, if not the catalyst directly, gave illuminants of a higher calorific value.

Table II. Comparison of Results of Catalyzed and Uncatalyzed Experiments under Comparable Oil Cracking Conditions,[a] but with Blue Gas Added in the Uncatalyzed Experiment

Experimental Conditions	Uncatalyzed + Blue Gas	Catalyzed
Temperature, ° F.	1600	1600
Mass velocity of steam,[b] lb./sq. ft. free cross section/hr.	11.4	9.7
Mass velocity of oil,[b] lb./sq. ft. free cross section/hr.	13.7	12.4
Total gas issuing from cracking tube, cu. ft./gal.[c]	191.1	184.7
Blue gas added, cu. ft./gal.	103.7	0.0
Thermal yield from oil gas, B. t. u./gal.	69500	69200
Illuminants, cu. ft./gal.	13.8	12.2
Methane, cu. ft./gal.	32.5	31.2
Ethane, cu. ft./gal.	0.9	1.3
Carbon in oil gas, mole/gal.	0.190	0.179
Steam per gal. oil, lb.	6.6	6.1
Steam decomposition, %	14	46

[a] The results given in this table are not directly comparable with those set forth in the curves, owing to a change in the amount of refractory surface used.

[b] Free cross-section area = 0.00181 square foot; volume of free space = 0.00212 cubic foot.

[c] All gas yields are expressed as cubic feet of dry gas at 60° F. and 29.92 inches of mercury.

Table III. Variation in Composition of Illuminants with Temperature

Temp.	No Catalyst Present			Sodium Carbonate Present		
	Compn.	H/C	Heating value	Compn.	H/C	Heating value
° F.			B. t. u./cu. ft.[a]			B. t. u./cu. ft.[a]
1300	$C_{2.7}H_{5.6}$	2.07	2159	$C_{2.7}H_{5.4}$	2.00	2120
1400	$C_{2.4}H_{5.0}$	2.08	1934	$C_{2.5}H_{4.6}$	1.84	1900
1500	$C_{2.3}H_{4.4}$	1.91	1799	$C_{2.4}H_{4.3}$	1.79	1851
1600	$C_{2.6}H_{5.1}$	1.96	2021	$C_{3.0}H_{5.3}$	1.77	2253

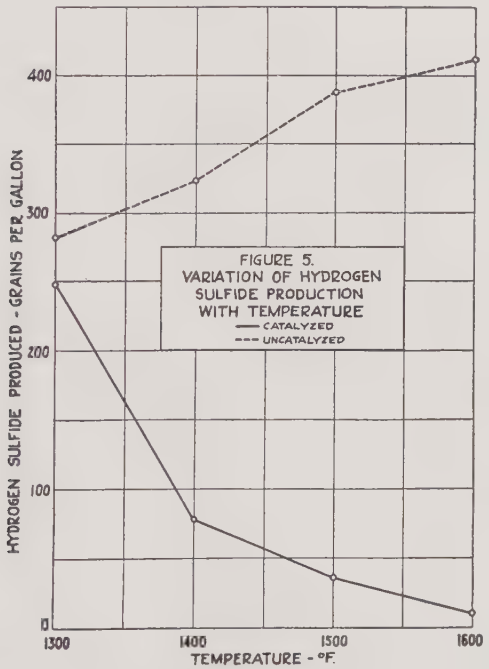
[a] At 60° F. and 29.92 inches of mercury.

Production of Sulfur Compounds

Decomposed in the uncatalyzed experiments, the oil gave an increasing amount of hydrogen sulfide with increasing temperatures. When the refractory surfaces were impregnated with soda, a marked decrease in the quantity of hydrogen sulfide resulted, and this quantity decreased with increasing temperatures. The observations are shown in Figure 5.

Since the alkali carbonate would be expected to decrease the production of hydrogen sulfide somewhat, an experiment was designed using refractory blocks which were impregnated with sodium sulfide. A comparison of the results thus obtained with those obtained in an analogous experiment in which sodium carbonate was used is shown in Table IV. These data suggest that refractories impregnated with the sulfide are just as active as those impregnated with the carbonate under the conditions encountered.

To determine whether this might be explained by a conversion of the sulfide to the carbonate under the conditions of the experiment, the refractory blocks from the sulfide were leached with water for about 48 hours. The filtered extract was very



dark green, suggesting the presence of colloidal ferrous sulfide, and considerable iron was found to be present. Iron was also found in the water extract obtained from refractories initially impregnated with sodium carbonate. The colloidal ferrous sulfide may have originated from the iron in the cracking tube, or in the refractory, or both.

Brief consideration of the equilibria involved will indicate that the conditions set up are very complex, and that, until further information is available, conclusions concerning the conversion and distribution of the sulfur and its effect upon the catalytic process should be somewhat tentative.

For such further studies, one desirable preliminary sim-

plification would be the elimination of sulfide-forming metals other than the catalyst from the reaction system. When the experiments involve the presence of iron, however, it may be said that the alkali exerts an appreciable influence on the production of hydrogen sulfide.

TABLE IV. COMPARISON OF RESULTS OBTAINED WITH REFRACTORIES IMPREGNATED WITH SODIUM CARBONATE AND WITH SODIUM SULFIDE[a]

EXPERIMENTAL CONDITIONS	UNCATALYZED	Na_2CO_3 CATALYST	Na_2S CATALYST
Temperature, ° F.	1600	1600	1600
Mass velocity of steam,[b] lb./sq. ft. free cross section/hr.	7.2	9.7	11.7
Mass velocity of oil,[b] lb./sq. ft. free cross section/hr.	12.8	12.4	13.7
Total carbon in gas, mole/gal.	0.180	0.312	0.309
Total gas, cu. ft./gal.	85.7	184.7	189.2
Blue gas, cu. ft./gal.	18.2	109.3	120.1
Oil gas, cu. ft./gal.	66.1	73.3	66.1
Total thermal yield, B. t. u./gal.	70100	101800	99800
Thermal yield from blue gas, B. t. u./gal.	5300	32600	35100
Thermal yield from oil gas, B. t. u./gal.	64800	69200	64700
Steam per gal. oil, lb.	4.4	6.1	6.7
Steam decomposition, %	11	46	46
H_2S produced, grains/gal.	343	148	170

[a] The results given in this table are not directly comparable with those set forth in the curves, owing to a change in the amount of refractory surface used.

[b] Free cross-section area = 0.00181 square foot; volume of free space = 0.00212 cubic foot.

In some of the experiments, the organic sulfur concentration of the gas was determined, and the organic sulfur formed appeared to vary with the amount of carbon deposited in the pyrolysis. Because of the disturbing influence of the iron, such observations are only tentative and should be further investigated. It has, however, been found in the industry that the organic sulfur formation can be decreased by maintaining low carbon conditions on the refractories (*7*, *10*), and this decrease can be explained by the carbon-sulfur complex theory (*5*).

CONCLUSIONS

When the refractory was impregnated with soda, at the higher temperatures of water-gas carburetion and at low rates of gasification, the experiments showed: (1) a pronounced increase in the gasification of the oil carbon and a corresponding decrease in carbonaceous deposits; (2) a decrease in the heating value of the gas per unit volume; (3) decided increases in the total thermal yield; (4) no marked primary effect upon the pyrolytic reactions; (5) the production of illuminants which were predominantly olefinic in character and of a higher calorific value; and (6) a decreased production of gaseous sulfur compounds, the last possibly because of an increased secondary reaction with the iron present. An experiment using sodium sulfide showed that this gave good catalytic activity under the conditions studied.

These results are definitely encouraging and suggest a

number of interesting phases for further study in relation to water-gas manufacture.

It must be noted, however, that for routine commercial work in both producer-gas and water-gas making, sodium compounds possess a disadvantage because of the marked volatility of this metal at the reaction temperatures. Another resides in the marked slagging effect of the alkaline compounds upon the fire-brick refractories ordinarily employed. While the latter may perhaps be overcome by the proper choice of an alkaline refractory, the loss of sodium due to the first suggests that the industry's attention might well be directed, in the present state of our knowledge, at least, to such matters as the presence of naturally occurring alkali bases in oils and coals.

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Biography

Martin Anderson Elliott, son of Walter Ward and Lillian (Kesmodel) Elliott, was born in Baltimore, Maryland, on February 21, 1909.

He attended the grade schools in Baltimore and later the Baltimore Polytechnic Institute from which he was graduated in June, 1927. He entered the Johns Hopkins University in September, 1927 and received the degree of Bachelor of Engineering in Gas Engineering in June, 1930. During his undergraduate residence, he was the holder of a Trustees' Scholarship. His work for an advanced degree was begun in the Department of Gas Engineering at the Johns Hopkins University in September, 1930.

During the summers of 1928, 1929, and 1931 he was employed as superintendent's aide in the Spring Gardens plant of the Consolidated Gas Electric Light and Power Company of Baltimore. In the summer of 1930 he was engaged under the direction of Dr. Lloyd Logan of the Department of Gas Engineering at the Johns Hopkins University in a study of the scientific and economic factors entering into the production and distribution of certain proposed gas mixtures.

While working for his advanced degree he was appointed a member of the teaching staff of the Department of Gas Engineering at the Johns Hopkins University, first as Laboratory Assistant for the term 1930–1931 and later as Junior Instructor for the terms 1931–1932 and 1932–1933. He is at present serving in the latter capacity.

He is a member of the American Chemical Society and Sigma Xi.